

applications, for example, hydrotreating, denitrification of waste gas, hydrogenation of CO, and the like.

The catalyst metals which can be deposited on the layered porous titanium oxide of this invention as a catalyst carrier include tungsten, molybdenum, cobalt, nickel, ruthenium, palladium, platinum, phosphorus, boron, and vanadium and a suitable combination of these catalyst metals can also be used. The method for depositing the catalyst metal is not restricted and any publicly known method can be adopted; for example, impregnation, ion exchange, and kneading. It is also possible to prepare a catalyst by depositing a catalyst metal on layered porous titanium oxide by an ion exchange method before the calcining step and then subjecting to the calcining step.

Moreover, titanium oxide itself has a photocatalytic ability as displayed in photooxidative decomposition and photoinduced superhydrophilicity and the layered porous titanium oxide of this invention which has a regulated pore structure, a large specific surface area, and excellent mechanical strength can be used by itself as a photocatalyst of high catalytic activity in various fields such as deodorization, water treatment, antibacterial treatment, and prevention of fouling.

Brief Description of the Drawings

Fig. 1 is a chart showing the results of X-ray diffraction performed on the layered porous titanium oxide prepared in Example 1.

diffraction performed on the specimens of layered porous titanium oxide respectively prepared in Comparative Example 16 and Example 5.

Fig. 14 is a graph showing the relationship between the content of titania and the mechanical strength (SCS) for the molded articles of alumina/titanium oxide prepared respectively in Examples 5-10 and Comparative Examples 7-11.

Fig. 15 is a graph showing the catalytic activity in the hydrodesulfurization test of vacuum gas oil (VGO).

Fig. 16 is a graph showing the catalytic activity in the hydrodesulfurization test of gas oil.

Fig. 17 is a graph showing the content of titania and the titania-localization index of the molded articles of alumina/titanium oxide prepared respectively in Examples 5-10 and Comparative Examples 7-11.

Preferred Embodiments of the Invention

This invention will be described concretely below with reference to the accompanying examples, comparative examples, and test examples. In the following description, " part" or "%" is on the mass basis unless otherwise noted and "L" stands for liter.

[Examples 1-4 and Comparative Examples 1-6]

Example 1

[pH swing step 1]

An alumina hydrogel (inorganic oxide) to be used as a core was prepared as follows.

calcined in an oven at 500 °C for 3 hours to give layered porous titanium oxide of Comparative Example 7 and its properties are shown in Table 3.

Example 5

Layered porous titanium oxide of Example 5 was prepared as in Comparative Example 7 with the exception of adding 1.8 parts of the colloidal silica and 65.0 parts of the 37.9% titanium tetrachloride solution and its properties are shown in Table 3.

Examples 6-10

The specimens of layered porous titanium oxide of Examples 6-10 were prepared as in Example 5 with the exception of adding 2.7 parts of the colloidal silica and changing the added amount of the 37.9% titanium tetrachloride solution from example to example, that is, 77.0 parts in Example 6, 101.0 parts in Example 7, 126.0 parts in Example 8, 155.0 parts in Example 9, and 189.0 parts in Example 10. Their properties are shown in Table 3.

Comparative Examples 8-10

The specimens of layered porous titanium oxides of Comparative Examples 8-10 were prepared as in Example 5 with the exception of adding 2.7 parts of the colloidal silica and changing the added amount of the 37.9% titanium tetrachloride solution from example to example, that is, 235.0 parts in Comparative Example 8, 310.0 parts in Comparative Example 9, and 465.0 parts in Comparative Example 10. Their properties are shown in Table 3.

As is shown in Fig. 14, the side crushing strength (SCS) is 0.5 kg/mm or more for the specimens of Comparative Example 7 and Examples 5-10, but it is 0.5 kg/mm

or less for the specimens of Comparative Examples 8-10 or a strength not strong enough for use in commercial catalysts.

Example 11

Layered porous titanium oxide of Example 11 was prepared as in Example 5 with the exception of using the silica hydrogel obtained in the pH swing step 2 to be described below in place of the alumina hydrogel as an inorganic oxide, using 1250 parts of the dispersion of silica hydrogel, omitting the addition of the particle growth inhibitor and the pH adjusting agent, and adding 73.3 parts of the 37.9% titanium tetrachloride solution and ammonia water at pH 4 between the isoelectric point of silica and that of titanium oxide. The properties of this layered porous titanium oxide are shown in Table 3.

[pH swing step 2]

In a 16-L enamel container was placed 4 L of a solution of sodium silicate (JIS No. 3) with a concentration of 100 g/L, the solution was heated at 50°C with stirring, a 20% sulfuric acid solution was added to bring the pH to 4, and the mixture was maintained for 5 minutes to give a slurry of silica hydrogel. Following this, the operation consisting of adding 320 ml of a sodium silicate solution with a concentration of 250 g/L to the slurry to change the pH to 11, maintaining the mixture for 10 minutes, then adding

Thereafter, the operation consisting of adding 180 g of the solution A to change the pH to 2.5, maintaining the mixture for for 5 minutes, again adding 180 g of the solution B to change the pH to 9, and maintaining the mixture for 5 minutes was repeated 3 times.

The alumina thus obtained was washed with water, filtered, molded, and dried at 120°C for 3 hours. The molded article was further calcined as in Comparative Example 7 to give a molded article of alumina of Comparative Example 16. The properties of this molded article of alumina are shown in Table 3.

The main peak of titanium oxide (anatase) was detected at $2\theta = 26.5^\circ$ and the peaks of alumina at 46.0° and 67.0° when the specimen of Comparative Example 16 was measured by X-ray diffraction, but these peaks are not detected clearly in Example 5. This indicates that the crystals of titanium oxide on the surface are too small to be detected by X-ray or they are amorphous in Example 5. A comparison of the results of X-ray diffraction conducted in Comparative Example 16 and Example 5 is shown in Fig. 13. As in Example 5, the peaks of titanium oxide were not observed in Comparative Example 7 and Examples 6-11.

[Evaluation tests]

The specimens obtained in the aforementioned Examples 5-11 and Comparative Examples 7-16 were evaluated according to the test methods to be described below.

(Definition of titanium localization index)

The amounts of aluminum (M) and titanium (Ti) are respectively measured by the use of an X-ray photoelectron spectrometer (XPS: JPS-9010 available from JEOL Ltd.) under the following conditions and the proportion of titanium (Ti) to the sum of aluminum (M) and titanium (Ti) or $B = \text{TiXPS} / (\text{TiXPS} + \text{M XPS})$ was calculated.

the test for hydrodesulfurization of VGO is graphically shown in Fig. 15 with the activity of the catalyst prepared from the specimen of Comparative Example 16 taken as 100.

It is seen from the results that the catalysts of this invention (prepared from the specimens of Examples) show activity comparable to that of titanium oxide alone of Comparative Example 11 and the properties inherent in titanium oxide are fully manifested. In Comparative Example 7, however, there is a shortage of titanium oxide to fully cover the alumina core and the desulfurization activity here does not differ very much from that of alumina alone.

(Test for hydrodesulfurization of gas oil)

The hydrodesulfurization of gas oil was performed in a high-pressure flow type reactor under the following conditions: reaction pressure, 5 MPa; reaction temperature, 360 °C; liquid hourly space velocity, 2.0 hr⁻¹; ratio of hydrogen to feedstock, 250 Nl/l. The catalysts submitted to the test were all treated for sulfidation in advance with gas oil whose sulfur content had been adjusted to 2.5% by addition of dimethyl disulfide. The activity of each catalyst obtained in the test for hydrodesulfurization of VGO is graphically shown in Fig. 16 with the activity of the catalyst prepared from the specimen of Comparative Example 16 taken as 100.

It is seen from the results that the catalysts of this invention (prepared from the specimens of Examples) show activity comparable to that of titanium oxide alone of Comparative Example 11 and the properties inherent in titanium oxide are fully manifested. In Comparative Example 7, however, there is a shortage of titanium oxide to fully cover the alumina core and the desulfurization activity here does not differ very much from that of alumina alone.

The titanium localization index defined in this invention is stipulated to be 1.6 or more and this means, as illustrated in Fig.17, that the surface

cannot be covered fully with titania when the Ti content is less than 10% while the proportion of alumina decreases with a concomitant drop in mechanical strength to below 0.5 kg/mm or below the strength required for practical use when the Ti content is more than 60% as shown in Fig. 14. Moreover, when the Ti content is more than 60%, titania increases in amount and tends to associate and become crystalline and there is the possibility of alumina not being covered satisfactorily.

[Table 3]

	Composition	Depositing operation	Titanium localization index (B/A)	Specific surface area (m^2/g)	Mechanical strength (SCS) (kg/mm)	X-ray diffraction	Raman spectroscopic analysis	Pore sharpness degree (%)	VGO-HDS Activity	GO-HDS Activity
Example 5	15%-TiO ₂ /Al ₂ O ₃	Between isoelectric points	1.94	331	1.12	Al	Amorphous	80	145	144
" 6	20%-TiO ₂ /Al ₂ O ₃		2.83	348	1.1	Al	Amorphous	78	148	152
" 7	30%-TiO ₂ /Al ₂ O ₃		2.57	380	0.95	Al	Amorphous	79	—	—
" 8	40%-TiO ₂ /Al ₂ O ₃		2.28	338	0.75	Al	Amorphous	72	—	—
" 9	50%-TiO ₂ /Al ₂ O ₃		1.92	286	0.6	Al	Amorphous	66	140	144
" 10	60%-TiO ₂ /Al ₂ O ₃		1.64	249	0.5	Al	Amorphous	55	—	—
" 11	20%-TiO ₂ /SiO ₂		1.92	385	0.96	Si	Amorphous	75	—	—
Comparative example 7	10%-TiO ₂ /Al ₂ O ₃	Between isoelectric points	1.58	326	1.15	Al	Amorphous	80	108	105
" 8	70%-TiO ₂ /Al ₂ O ₃		1.38	212	0.45	Al+Ti	Anatase	49	—	—
" 9	80%-TiO ₂ /Al ₂ O ₃		1.23	189	0.35	Al+Ti	Anatase	48	—	—
" 10	90%-TiO ₂ /Al ₂ O ₃		1.13	178	0.3	Al+Ti	Anatase	47	—	—
" 11	100%-TiO ₂	—	1.00	160	0.25	Ti	Anatase	63	150	160
" 12	20%-TiO ₂ /Al ₂ O ₃	pH \leq 6	1.15	258	1.1	Al+Ti	Anatase	52	108	106
" 13	20%-TiO ₂ /Al ₂ O ₃	pH \leq 6 PHS	1.13	243	1.1	Al+Ti	Anatase	55	—	—
" 14	20%-TiO ₂ /Al ₂ O ₃	pH \geq 9	1.18	247	1.1	Al+Ti	Anatase	51	—	—
" 15	20%-TiO ₂ /Al ₂ O ₃	Physical mixing	1.08	274	0.8	Al+Ti	Anatase	32	110	105
" 16	100%-Al ₂ O ₃	—	—	320	1.2	Al	—	84	100	100

Note : The proportion of TiO₂ in the composition denotes the amount of deposited TiO₂, VGO-HDS denotes the catalytic activity in the hydrodesulfurization of vacuum gas oil, and GO-HDS denotes the catalytic activity in the hydrodesulfurization of gas oil.

What is claimed is:

1. (As amended) Layered porous titanium oxide comprising an inorganic oxide as a core and titanium oxide deposited on the surface of the inorganic oxide wherein the titanium localization index (B/A) represented by the ratio of the proportion of titanium (Ti) to the sum of the constituent metal (M) of the inorganic oxide and titanium (Ti) determined by X-ray photoelectron spectroscopy (XPS) [$B = \text{Ti XPS} / (\text{Ti XPS} + \text{M XPS})$] to the bulk mixing molar ratio of titanium (Ti) to the sum of the constituent metal (M) of the inorganic oxide and titanium (Ti) [$A = \text{Ti} / (\text{Ti} + \text{M})$] is 1.6 or more, the repeat distance between the crystal lattice planes of titanium oxide on the surface of the inorganic oxide is 50Å or less, and the titanium oxide is deposited on the surface of the inorganic oxide so as to be chemically and/or microscopically united to the inorganic oxide.

2. Layered porous titanium oxide as described in claim 1 wherein the amount of deposited titanium oxide is 13-60 mass%.

3. (Deleted)

4. Layered porous titanium oxide as described in any one of claims 1 to 3 wherein the pore sharpness degree is 50% or more.

5. Layered porous titanium oxide as described in any one of claims 1 to 4 wherein the pore volume is 0.3 mL/g or more.

6. Layered porous titanium oxide as described in any one of claims 1 to 5 wherein the specific surface area is 100 m²/g or more.

7. Layered porous titanium oxide as described in any one of claims 1 to 6 wherein the inorganic oxide is a hydrosol, a hydrogel,

a xerogel, a hydroxide, or a hydrated oxide and the titanium oxide is deposited on this organic oxide.

8. Layered porous titanium oxide as described in any one of claims 1 to 7 wherein the inorganic oxide is synthesized by the pH swing operation.

9. Layered porous titanium oxide as described in any one of claims 1 to 8 wherein the inorganic oxide is at least one selected from the group of alumina, silica, magnesia, silica/alumina, silica/titania, alumina/zirconia, silica/zirconia, and silica/magnesia.

10. Layered porous titanium oxide as described in any one of claims 1 to 9 wherein the inorganic oxide is needle-shaped or column-shaped.

11. Layered porous titanium oxide as described in any one of claims 1 to 10 wherein layered porous titanium oxide is obtained in the depositing step which comprises supplying a raw material titanium solution and a pH adjusting agent in the presence of an inorganic oxide and depositing titanium oxide on the surface of the inorganic oxide in the pH range between the isoelectric point of titanium oxide and that of the inorganic oxide.

12. Layered porous titanium oxide as described in claim 11 wherein the layered porous titanium oxide is obtained by the calcining treatment performed in the temperature range of 90-900 °C after the depositing step.

13. A process for producing layered porous titanium oxide comprising an inorganic oxide as a core and titanium oxide deposited on the surface of the inorganic oxide which comprises

a depositing step for supplying a solution of titanium chloride, titanium sulfate, or titanyl sulfate in the presence of an inorganic oxide and a pH adjusting agent in the presence of an inorganic oxide and depositing titanium oxide on the surface of the inorganic oxide in the pH range between the isoelectric point of titanium oxide and that of the inorganic oxide.

Fig. 14

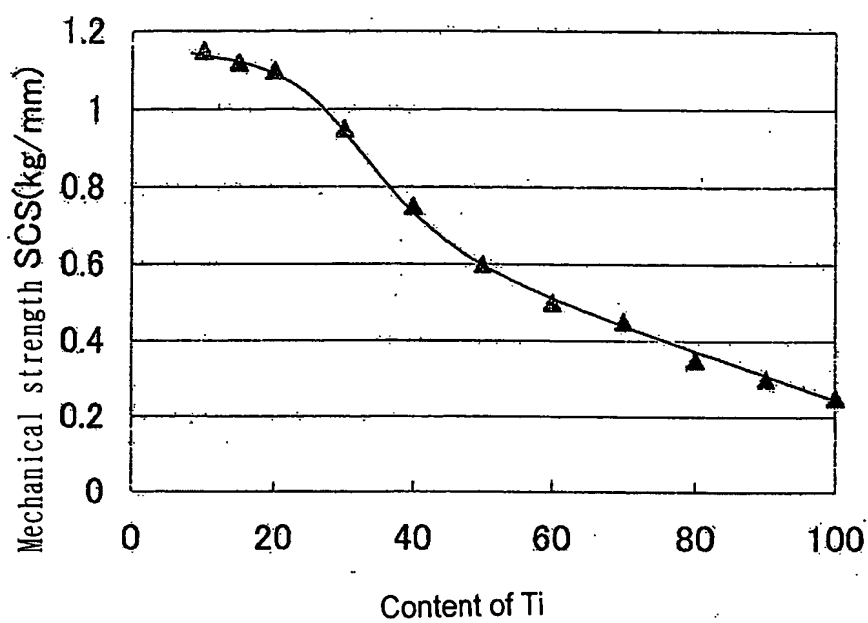


Fig. 15

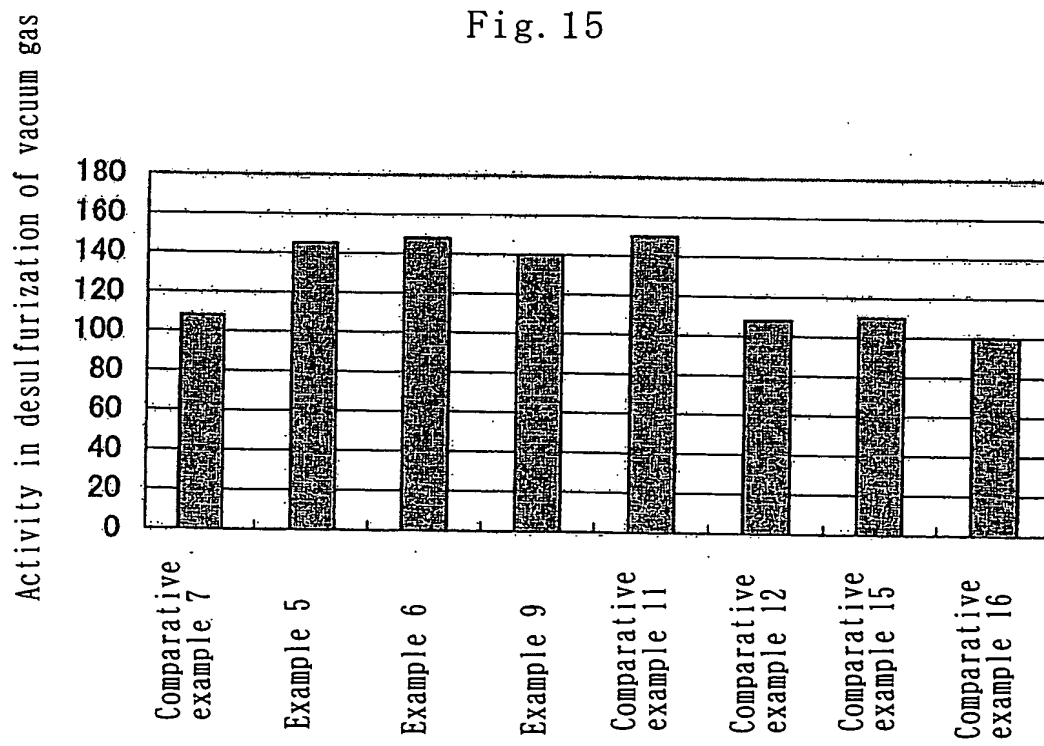


Fig. 16

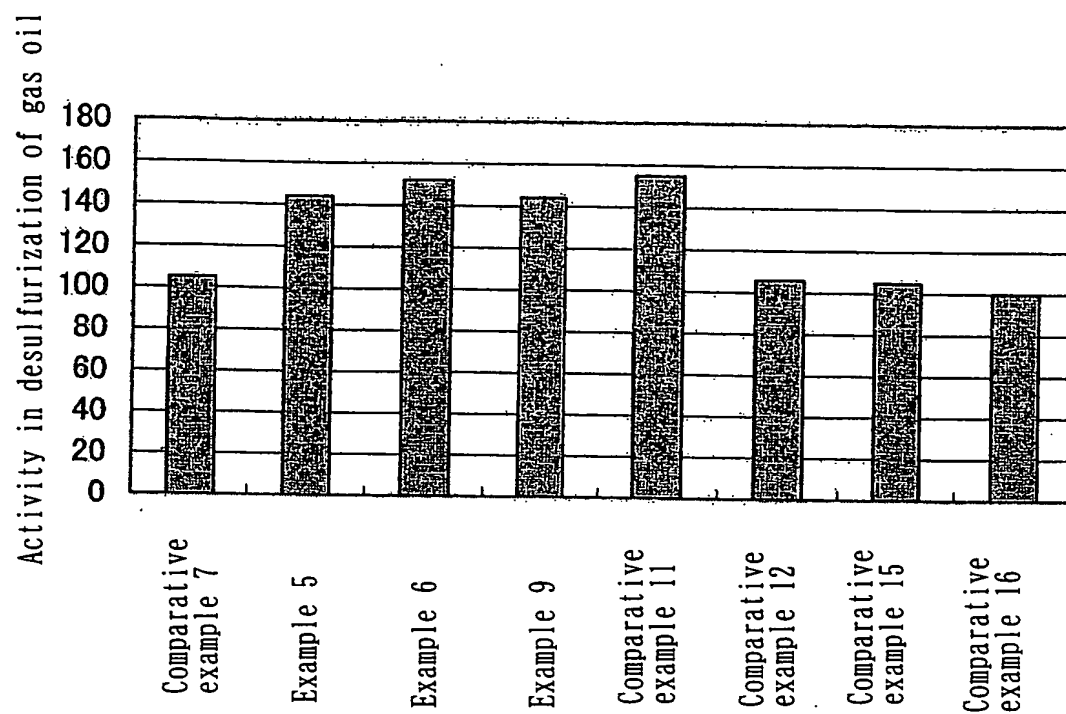


Fig. 17

